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FORENSIC COMPARISONS OF SOILS BY NEUTRON ACTIVATION AND ATOMIC ABSORPTION ANALYSIS

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Laboratories conducting physical evidence examinations are often called upon to examine soils to determine whether questioned and known specimens have a common origin. Although much information about this type of sample can be obtained by well established physical and wet-chemical methods, these analyses alone provide little information about their individuality.

Since soil is vastly complex and contains all the minerals occurring on earth, it is reasonable to assume that this material can be characterized by measuring the distribution of a sufficient number of elements, especially those which are present in trace quantities and not commonly found in all specimens. Soil scientists have known for many years that this material exists in a state of dynamic equilibrium with its environment—i.e., it is constantly undergoing a slow change as new soil is formed and old soil is removed. The weathering action of wind, water, heat, and cold is constantly altering its inorganic and organic composition. Plant and animal life as well as geological factors lend individuality to soil. Man is constantly altering the composition of soil through industrial by-products such as sewage wastes, land fill projects, and crop fertilization.

The individualization of a material constantly being altered by its environment can be accomplished with reliability if a sufficient number of identifying characteristics are determined. Some points of identification can be obtained through the use of physical methods¹ and chemical procedures for the determination of major mineral

constituents². During the past few decades instrumental techniques such as spectrophotometry, x-ray diffraction, and emission spectrography have been developed to the point of forensic acceptability and provide the analyst with additional methods of analysis.

Since neutron activation analysis and atomic absorption are well developed analytical techniques and have been shown to be feasible for the characterization of various types of physical evidence³ their application to the problem of measuring the trace elemental distribution in soil specimens was evaluated. In this study advantage was taken of the extreme sensitivity of these techniques for the measurement of a large number of elements and after measurement, the statistical significance of the distribution of these elements was assessed.

EXPERIMENTAL

Collection areas were selected in the states of Georgia, Texas, and Washington, and surface soils were taken according to the pattern shown in figure 1.

Since surface soils are those most frequently encountered in forensic work, about $\frac{1}{2}$ pound of sample was taken from each collection point at depths less than $\frac{1}{2}$ inch. These samples were dried

² BEAR, F. E., CHEMISTRY OF THE SOIL, Reinhold Publishing Company, New York, Sec. Ed. (1965).

³ BATE, L. C., EMERY, J. F., LEDDICOTE, G. W., LYONS, W. S., and PRO, M. J., 14 INTER. J. APPL. RADIATIONS AND ISOTOPES, 549 (1963).

BRYAN, D. E., and GUINN, V. P., 7 AM. NUCLEAR SOCIETY, 329 (1964).

SCOTT, J. E., HOFFMAN, C. M., PRO, M. J., and SCHLESINGER, H. L., 50 ASSOC. OF OFF. ANAL. CHEM., 371 (1967).

¹ LUNDQUIST, F., METHODS OF FORENSIC SCIENCE, Interscience Publishers, New York, Vol. I., p. 356-362 (1962).

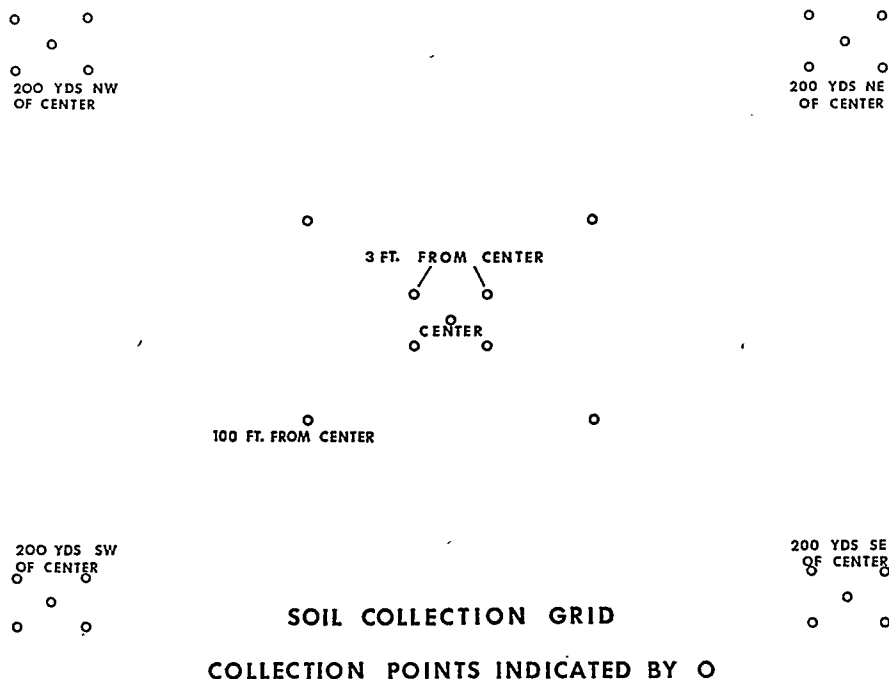


FIGURE 1

under infrared lamps, the lumps ground in an agate mortar and pestle, and the sample was then sifted through a 60 mesh standard sieve to remove stones and vegetable matter. The sieved portion of the samples was analyzed by both neutron activation analysis and atomic absorption.

NEUTRON ACTIVATION ANALYSIS

A 500 mg portion of each sample was irradiated for 10 minutes in a thermal neutron flux of about $10^{13}n/cm^2/sec$, and the induced radionuclides were measured by gamma-ray spectrometry without radiochemical separations. Longer periods of irradiations were investigated and were found to be undesirable because large quantities of 15 hour Na-24 are produced, and its gamma-ray spectra obscures the photopeaks from less abundant elements such as 12.8 hour Cu-64, 2.8 hour Sr-87 and 14 hour Zn-69M.

Neutron flux variations were monitored with pure copper standards simultaneously irradiated with each sample. Induced activities were then normalized to a reference neutron flux of $6.68 \times 10^{12}n/cm^2/sec$. To further minimize the effect of flux changes between successive irradiations, groups of five samples from the same location on the collection grid were simultaneously irradiated.

After irradiation the soils were transferred to non-irradiated plastic containers, and the gamma-ray emissions were measured with a 3" x 3" NaI (T1) crystal housed in a mercury filled stainless steel shield. In this work, a RIDL 34-12B 400 channel analyzer with Hewlett-Parkard printer and Mosley X-Y plotter was used for all measurements.

ATOMIC ABSORPTION

Samples weighing approximately one gram were placed into solution by the standard sodium carbonate fusion method. The silica was separated, and the filtrate analyzed for the elements present. A Jarrell-Ash model 82-500 atomic absorption apparatus with Westinghouse multi-element hollow cathode lamps was used. Measurements were made with 100 micron entrance and 150 micron exit slits. Aluminum was determined using a nitrous oxide acetylene fuel mixture with a laminar flow burner while all other elements reported in this work were measured using a hydrogen-air fuel mixture with a Hetco total consumption burner.

PRECISION STUDY

The characterization of soils, through their trace elemental distribution, was approached on a

Table 1
NEUTRON ACTIVATION ANALYSIS PRECISION STUDY

Element	Source	Average Concentration (PPM)	Average Deviation (PPM)	Percent Deviation	Average Precision
Chlorine	Georgia	9000	2700	±30.2	±3.7%
Manganese	Georgia	490	18	±3.6	
Manganese	Washington	570	36	±6.2	
Manganese	Texas	310	4	±1.4	±15.0%
Sodium	Georgia	520	160	±31.0	
Sodium	Washington	960	100	±10.6	
Sodium	Texas	310	11	±3.5	±5.2%
Scandium	Georgia	7.3	0.6	±8.2	
Scandium	Washington	22	1	±5.4	
Scandium	Texas	46	1	±1.9	±9.6%
Barium	Georgia	2450	250	±10.1	
Barium	Washington	Trace	not calculable	not calculable	
Barium	Texas	1050	96	±9.1	±14.2%
Lanthanum	Georgia	48	9.3	±19.4	
Lanthanum	Washington	Present	not calculable	not calculable	
Lanthanum	Texas	17	1.6	±9.0	±3.2%
Samarium	Georgia	1.02	0.01	±1.5	
Samarium	Washington	0.53	0.02	±3.8	
Samarium	Texas	0.46	0.02	±4.3	

statistical basis. For this reason, the analytical precision of the measurements used in this evaluation was determined by repetitive sample analysis.

The precision of neutron activation analysis, was ascertained by selecting one sample from the Georgia, Texas, and Washington collection area and analyzing each of these samples in triplicate. The results presented in Table 1 show the precision of the method for elements in this type of sample matrix. With the exception of sodium, the precision represented by the percent deviation is reasonably constant for the determination of a particular element in the soils analyzed from the different geographical sources. The average precision for each element was calculated from the average of the percent deviation observed in the soils from the three locations. For example, the percent deviation for manganese was ±3.6, ±6.2, and ±1.4 for the soils from Georgia, Washington, and Texas respectively. An average of ±3.7 percent was calculated.

The precision of the data obtained by the atomic absorption technique was determined by analyzing

Table 2
ATOMIC ABSORPTION ANALYSIS PRECISION STUDY

Element	Average Concentration (PPM)	Average Deviation (PPM)	Percent Precision
Potassium.....	24,200	600	±2.4
Aluminum.....	4,900	300	±6.5
Strontium.....	55	18	±33
Magnesium.....	1,900	200	±10
Lithium.....	24	0.8	±3.5
Rubidium.....	36	2	±5.8
Calcium.....	310	110	±36
Manganese.....	310	20	±5.5
Iron.....	14,000	1,000	±7.0
Nickel.....	140	6	±4.5
Chromium.....	53	6	±11
Copper.....	260	24	±9.2
Zinc.....	620	47	±7.5

a single soil sample in quadruplicate. Unlike purely instrumental neutron activation analysis, matrix effects are not serious in the analytical comparison of similar materials by this technique.

Table 3
ELEMENTAL CONCENTRATION RANGES

Area		% Iron	% Aluminum	% Potassium	PPM Nickel	PPM Zinc	PPM Lithium	PPM Rubidium
Georgia	Low	0.4	3.2	2.4	240	26	18	60
	High	1.9	10.7	11.1	430	65	50	140
Washington	Low	2.0	6.3	2.4	310	70	5	10
	High	2.7	8.2	8.0	380	130	30	17
Texas	Low	0.5	0.9	0.5	190	50	6	9
	High	1.3	2.2	2.0	350	400	16	32
Area		PPM Samarium	PPM Lanthanum	PPM Magnesium	PPM Scandium	PPM Sodium	PPM Manganese	PPM Copper
Georgia	Low	3	70	10	2	180	310	80
	High	80	370	2000	40	690	570	130
Washington	Low	4	12	10	18	8500	510	140
	High	40	40	19	23	10,300	700	210
Texas	Low	2.8	14	850	20	520	140	84
	High	7.8	32	2820	67	1130	530	600

Therefore, a sample from a single location was considered sufficient for the purpose of establishing the analytical precision for the measurement of each element.

The data presented in Table 2 shows that with the exception of calcium and strontium, each element could be measured with good precision.

ELEMENTAL DISTRIBUTION

Neutron activation analysis and atomic absorption were employed to determine the elemental composition of the 29 soils from each of the three collection areas selected for this study. Samarium, lanthanum, barium, protactinium, cesium, hafnium, scandium, sodium, chromium, and cerium were measured by neutron activation analysis, and copper, strontium, magnesium, calcium, manganese, aluminum, iron, nickel, zinc, lithium, rubidium, and potassium were determined by atomic absorption. These results showed that some of the elements were found in a wide concentration range over the sample grid while others remained fairly constant even in samplings 200 yards apart. Table 3 shows the elemental concentration range observed for each element in the Georgia, Texas, and Washington collection areas.

Although the soils taken from a three foot radius contain the same elements in approximately the

same concentrations, similar clusters of samples collected various distances from the center of each soil grid had different elemental compositions. This elemental distribution is shown in Table 4 in which the specimens from the Georgia collection are used as an illustration. The concentration of each element at the center and 200 yards from this center point represents the average of the results from the five samples within the radius of three feet.

The results from the analysis of the samples from each collection area were assessed to determine the variation in soil composition over the area of each collection grid. This was accomplished by determining the distribution range of each element and then subdividing this range into analytically distinguishable increments. Each increment was calculated on the basis of \pm three times the analytical precision for each element multiplied by the average concentration of that element in the appropriate collection grid. To illustrate; the average manganese concentration in the Georgia samplings is 616 PPM \pm 5.5% as determined by atomic absorption.

Then: (3) (\pm 5.5) = 16.5%

(616 PPM) (\pm 0.165) = 616 \pm 102 PPM

Or: A range of 500 PPM to 720 PPM

Table 4
ELEMENTAL DISTRIBUTION (Georgia Collection Site)
(PPM unless otherwise expressed)

	% Iron	% Aluminum	% Potassium	Nickel	Zinc	Lithium	Rubidium	Samarium	Lanthanum
Center.....	0.54	3.8	8.03	240	28	18	110	81	370
100 Ft. from center.....	0.62	3.44	6.77	250	33	21	128	28	160
200 Yds. North of center.....	0.68	6.39	11.1	290	40	28	260	6.8	100
200 Yds. South of center.....	0.42	1.58	2.4	260	26	15	61	2.9	70
200 Yds. East of center.....	1.87	10.7	4.07	430	65	50	140	39	90
200 Yds. West of center.....	1.06	7.26	4.79	300	46	20	116	44	150
	Cesium	Hafnium	Scandium	Sodium	Manganese	Copper	Strontium	Magnesium	
Center.....	ND	27	40	690	500	94	42	8.8	
100 Ft. from center.....	19	27	7.1	690	550	80	23	10.6	
200 Yds. North of center.....	2	13	3.7	730	310	132	23	11.1	
200 Yds. South of center.....	2	11	2.3	180	130	78	9.7	335	
200 Yds. East of center.....	2	9	12	390	570	160	32	1990	
200 Yds. West of center.....	2	9	18	690	510	83	16	1292	

The distinguishable concentration ranges for the other elements found in the three collection areas were calculated in a similar manner and the number of samples in each range was totaled. The probability of randomly selecting a sample from the grid which contains an element in a specific concentration range is the total number of samples in that concentration range, divided by the total number of samples in the sample grid.

The data shown in Table 5 illustrates the probabilities for each element measured in the 29 samples from the Georgia grid. Based on these probabilities, it is possible to estimate the chances of randomly selecting two samples containing the same elements in the same concentration ranges from the grid of 200 yard radius. The chance of selecting two samples containing 15 elements in the most common concentration ranges (lowest probabilities) is calculated by multiplying the factors for each of these elements. The product of this multiplication indicates that there is 1 chance in 190,000 of randomly selecting two matching samples from the collection grid.

It is obvious that the chance of finding two surface soils from different locations which contain the same 15 elements in the same concentrations would become increasingly smaller as the surface area of the grid increases. This is to say that the chance of finding two soils from different locations which have the same trace elemental composition is quite small.

DISCUSSION AND CONCLUSIONS

This work shows that soils collected over fairly short distances have a variation in trace elemental composition. It was shown that neutron activation analysis and atomic absorption are valuable adjuncts to the conventional methods of forensic soil examination. The many elements that can be determined by these techniques provide the points of identification necessary for the comparison of questioned and known soils.

It should be noted that in this control study, every effort was made to sample areas where small differences in trace element concentration would be expected. This was accomplished by collecting samples from relatively small flat areas which appeared to be uniform. Three times the analytical precision was used to establish the concentration ranges observed for each element, and only those ranges occurring most frequently for the elements were used to calculate the probability of randomly selecting two samples containing 15 elements in the same concentrations. Even with liberal probability factors, the variations in the soils connected with this study show that specimens from different locations can be distinguished.

These calculated probability factors are not applicable to all soil comparisons because it is necessary to establish the concentration ranges for each element from a particular collection area. Their use in this work is only to illustrate the

Table 5
 PROBABILITIES OF OCCURRENCE CALCULATED FOR GEORGIA SAMPLE GRID
 (For ease of tabulation, probabilities indicated are reciprocal values)

PPM Range Probability	PPM Range Probability	PPM Range Probability	PPM Range Probability	% Range Probability
Manganese	Magnesium	Samarium	Lithium	Potassium
43/247 5.8	0/127 1.9	0/8 3.6	8/16 3.6	1.70/2.66 5.8
248/352 30	128/368 30	9/25 5.8	17/25 2.4	2.67/3.63 30
353/557 3.2	369/608 7.2	26/42 4.8	26/34 9.7	3.64/4.59 5.8
558/762 5.8	609/848 30	43/59 5.8	35/43 9.7	4.60/5.55 5.8
763/966 30	849/1089 29	60/76 7.2		5.56/6.51 14
967/1170 7.2	1090/1330 29	77/93 30	Zinc	6.52/7.47 7.2
1171/1380 5.8	1331/1570 7.2	94/110 30	10/32 2.2	7.48/8.43 29
1381/1580 29	1571/1810 30	111/127 30	33/55 4.8	8.44/9.39 30
	1811/2050 14.5	128/144 30	56/78 5.8	9.40/10.3 14
	2051/2290 29	145/161 30		10.4/11.4 5.8
	2291/2531 29	162/178 29	Chromium	
Copper			3/19 1.7	
25/89 2.0			20/36 14	Aluminum
90/154 2.6			37/53 7.2	0/2.75 5.8
155/219 9.7				2.76/5.24 2.4
220/284 29				5.25/7.73 5.8
	Rubidium	Scandium	Lanthanum	7.74/10.2 9.7
	24/88 7.2	0/12 1.6	0/133 1.6	10.3/12.7 7.2
Nickel	89/152 1.8	13/25 4.8	134/400 2.6	
165/255 3.6	153/216 7.2	25/37 7.2	401/667 29	Iron
256/345 1.8	217/280 9.6	38/50 30		0.12/0.68 1.9
346/430 14	281/344 29	51/62 30	Sodium	0.69/1.25 3.2
431/525 9.7		63/75 29	0/320 4.8	1.26/1.82 14
			321/741 1.7	1.83/2.5 9.7
			742/1160 4.8	

magnitude of the differences in soil composition when a large number of trace elements in specific concentration ranges are employed as points of identification. In an actual case, where a limited number of soil samples are collected, an estimate of the probability of finding two soils from different locations with the same trace elemental composition may be expressed by a simplified relationship:

$$\text{Probability} = X^n$$

Where X = The average number of analytical distinguishable ranges for each element. (Approximately 5)

n = Number of elements measured

The five distinguishable concentration ranges in this expression represent the average number of concentration ranges found in the control studies. This is to say that each element measured in two soils from different locations has a chance of one in five that the element can be found in both soils in the same concentration. Admittedly, this calculation provides only an order-of-magnitude

answer to the often asked question "what are the chances of finding another sample with the same elements in the same concentrations but which comes from a different location".

In actual case work, an unusually high concentration of an element may serve to individualize a sample and enhance the forensic worth of the soil specimen. However, high concentrations of certain elements such as lanthanum, samarium, zinc, and antimony tend to obscure the spectra of other radioactive species when using gamma-ray spectrometry alone. This problem is well illustrated in the case of the U.S. vs. Horger, Leavell, and O'Berry⁴ in which soil comparisons were made to connect National Firearms violators with a stash of 500 tons of machine gun parts. In this case, large quantities of lanthanum limited the neutron activation analysis to the determination of five elements while the use of atomic absorption made it possible to quantitate an additional ten elements.

⁴United States vs. Horger, Leavell, and O'Berry U. S. Federal Court, Columbia, South Carolina, February 21 (1967).

The information obtained from both techniques established that soil on containers of machine gun parts in Horger's possession was the same as soil taken from the stash.

The methods used to examine the physical evidence in the above case illustrates that the use of multiple analytical techniques can very often provide the additional information needed for a

strong scientific conclusion. Although it is often possible to show that soils are dissimilar by microscopic examination or other procedures, in cases where similarity is indicated the combination of neutron activation analysis and atomic absorption analysis can provide the analyst with the information necessary to establish the common origin of soils.